

PROMOTED HYDROTREATING CATALYSTS

A. S. Hirschon, L. L. Ackerman, and R. B. Wilson
SRI International

Y. Horita and T. Komoto
Nippon Steel Chemical Corporation

Keywords: Hydrotreating, HDN, catalysts

INTRODUCTION

With dwindling supplies of high quality petroleum feedstocks, efforts are being taken to utilize alternative feedstocks such as heavy crudes and coal liquids as sources for chemicals and alternative fuels. However, these feedstocks are often heavily aromatic and contain large amounts of heteroatoms such as nitrogen, sulfur, and oxygen. Nitrogen and oxygen are so difficult to remove that extremely strenuous conditions are required. However, under these severe conditions the valuable aromatics are also excessively hydrogenated, wasting valuable hydrogen. Attempts to improve the current hydrotreating catalysts such as NiMo, CoMo, and NiW that have been developed for petroleum feedstocks have met with little success. What is needed are catalysts that are more selective toward hydrogenolysis activity rather than hydrogenation reactions. Therefore efforts are being conducted to find catalysts that can selectively remove heteroatoms, in particular, nitrogen. Workers have shown in systematic studies that for each row of the periodic table a correlation occurs between the position and the reactivity of the bulk metal towards hydrogenolysis reactions, with the lower rows being the most active.¹⁻⁴ Using this methodology, certain noble metals such as ruthenium have been identified as highly active hydrogenolysis catalysts.

Since the ratio of the hydrogenolysis to hydrogenation activity varies with the nature of the catalyst, various metals and metal combinations have been investigated in efforts to find catalysts with improved selectivity and high ratios of hydrogenolysis to hydrogenation activities.⁵⁻¹⁰ Recently it has been shown that when ruthenium was used in conjunction with molybdenum, a very active and selective hydrodenitrogenation catalyst was formed. In this work we investigated several methods of preparation of this catalyst and their respective activities towards both model systems and coal tars.

EXPERIMENTAL

Catalyst Preparation

Alumina extrudates were used for coal tar testing whereas powdered alumina was used for the model system testing. Molybdenum and nickel salts were impregnated into the alumina by standard incipient wetness techniques. Ruthenium was added as the carbonyl for the majority of the catalysts; the methodology for incorporation of ruthenium and activation of the catalyst is described in the text.

Catalyst Testing

The catalysts were evaluated for HDN and HDO using quinoline and diphenylether, respectively. Under nitrogen, 0.100 g of catalyst, 10 mL of a 0.197 M quinoline, and 0.086 M n-tetradecane (internal standard) and/or 0.150 M diphenyl ether were placed in a quartz liner in a 45-mL Parr bomb. The Parr bomb was pressurized with 500 psig of H₂ and heated for the desired times and

temperatures. The quinoline and the diphenyl ether were used to compare the catalysts for HDN and HDO activities, respectively. The HDN reactions were run at 350°C, and the HDO reactions were run at 250° to 300°C. The competitive HDN/HDO reactions were run at 350°C.

The HDN activities of the catalysts were compared by calculating the turnover frequencies (TF) for the disappearance of tetrahydroquinoline (THQ) and formation of propylbenzene (PB) and propylcyclohexane (PCH). Selectivities were determined from the relative distribution of PCH, PB, and propylcyclohexene (PCHE) when 5% of quinoline had been converted to these hydrocarbon products. HDO activities were compared by calculating the TF for the disappearance of diphenyl ether (DPE) and appearance of cyclohexane and benzene. HDO selectivities were determined from the relative proportions of benzene, cyclohexane, and phenol at a given level of conversion.

The activities of the catalysts were evaluated for the hydrotreatment of coal tars using a continuous flow reactor with 20 mL of catalyst at 360°C, 180Kg/cm² pressure hydrogen and LHSV of 0.5h⁻¹. The reaction was monitored by elemental analysis of the product stream with samples taken after 100 h on-stream.

RESULTS AND DISCUSSION

Hydrogenolysis of Model Compounds

Since both nitrogen and oxygen containing molecules cause the most problems in upgrading coal derived liquids, both HDN and HDO reactivities on model systems were investigated. A summary of the effect of ruthenium promotion of supported NiMo and CoMo alumina catalysts on the HDN reaction of quinoline (Table 1) shows that the promoted CoMo gives exceptional performance; even greater than that of promoted NiMo under these conditions. Furthermore, the promotion shows a large increase in selectivity for the CoMo system from a PCH/PB ratio of 15:1 to 3:1, compared to an increase of 4.9:1 to 2.6:1 for the NiMo system. However, when the RuCoMo catalyst was examined for the HDO of diphenylether, the CoMo catalysts was actually found to be more reactive; but when examined in a competition study with both quinoline and diphenylether present, the reverse order was found and the promoted RuCoMo catalyst was both the most active and selective catalyst. Apparently the amine reduced the HDO activity of the CoMo catalyst to a greater extent than the RuCoMo catalyst. Thus we would expect that the ruthenium promoted catalysts would be most useful in hydrotreating coal liquids and other alternative fuels.

Method of Activation and Preparation

The procedure we used for the formulation of the ruthenium promoted catalyst involved presulfiding the molybdenum based catalyst and then adding ruthenium carbonyl. The objective of this synthesis was to add the ruthenium to the sulfidryl groups of the sulfided metal (molybdenum for instance). This procedure was based on the methods of Yermakov, and was designed to produce a highly dispersed mixed metal cluster.¹¹ However, in common practice catalysts are not sulfided as an intermediate step, and therefore we varied the order of sulfiding and calcining as follows, to determine if there would be any effects on the activities and selectivities of these ruthenium promoted catalysts. Promoted molybdenum catalysts were prepared by three different methods. Method 1 consisted of impregnating the molybdenum catalyst with the ruthenium carbonyl in THF, evaporating the THF, and then first calcining and then sulfiding the product at 400°C. The method is similar to a conventional catalyst preparation, where each metal is sequentially added and calcined. The calcination step assures that the metals interact with the

support for high dispersion and to prevent loss of metal during use. Method 2 consisted of sulfiding the RuMo product without the second calcining step. In Method 3, we prepared the catalyst our normal way, first sulfiding the molybdenum catalyst and adding the ruthenium to the sulfided molybdenum catalyst, and then sulfiding again.

The activities and selectivities of the catalysts prepared by these methods are listed in Tables 3 and 4 for HDN reactions using quinoline as a model system. As seen in these tables, the selectivity of the catalyst produced by method 1 is high, giving a PCH/PB ratio of 3.0, but the overall activity is much lower than that for the other two methods, having a rate almost 200 times less active than for method 3. As seen for Methods 2 and 3, the activities are greatly improved, with method 3 being the most active for HDN activity. We believe that the difference between the activities is due to the sulfiding of the molybdenum prior to the promotion with Ru. Thus method 1 should give strong Al-O-Ru interactions, whereas method 3 should give Mo-S-Ru interactions, which we postulate will allow a synergy between the Mo and Ru.

Testing of Catalysts on Coal Tars

In order to verify these results on model systems, samples of RuCoMo, RuNiMo, and RuMo were evaluated for hydrotreating of coal tars. Table 5 lists some of these results. As seen from this table, there were both similarities and differences from the results on the model systems. For instance, the promotion of the CoMo catalyst (2A) to form RuCoMo (2B) gave little difference in the HDN of the coal tar (HDN rates of 0.47 and 0.44, respectively). However, promotion of the CoMo catalyst gave a very dramatic increase in reactivity and selectivity for quinoline HDN. In contrast, the promotion of NiMo (1A) with ruthenium to form RuNiMo (1B) did indeed increase the reactivity towards coal tars, and increasing both the rate of nitrogen removal (from 0.43 to 0.55) as well as increasing the selectivity of HDN to hydrogenation reactions. Catalyst 3A and 3B were RuMo catalysts designed to compare the method of preparation as previously described in the model systems. Catalyst 3A was prepared by first sulfiding the molybdenum and then adding ruthenium (Method 3), and 3B was prepared by adding the ruthenium to the calcined molybdenum, calcining again, and then sulfiding (Method 1). Again, as with the model systems, the presulfiding increased the activity of the catalyst.

CONCLUSIONS

Ruthenium promotion enhances HDN activity under low-severity hydrotreating of coal tars, confirming our previous studies with model systems. Promotion of CoMo is not as effective on coal tars as with model systems, and may depend upon the type of feedstock. However, promotion of NiMo gave enhanced HDN activity and selectivity for both systems. The key to the high activity and selectivity appears to be adding the ruthenium to a previously sulfided molybdenum catalyst. The reason for this high activity, we believe, is the formation of a Ru-S-Mo interaction, which may allow a better synergistic relationship. However, alternative explanations may be possible, and a more detailed study of these catalysts may lead to a better description of the active site.

REFERENCES

1. H. Sinfelt, *Prog. Sol. St. Chem.* (1975), **10**, 55-69.
2. T. A. Pecoraro and R. R. Chianelli, *J. Catal.* (1981), **67**, 430

3. S. Harris and R. R. Chianelli, *J. Catal.* (1984), 86, 400-412.
4. A. S. Hirschon and R. M. Laine, *Energy and Fuels*, (1988), 2, 292-295.
5. A. S. Hirschon, R. B. Wilson, Jr. and R. M. Laine, *Amer. Chem. Soc. Div. Pet. Prepr.* (1987), 32(2), 268-270.
6. A. S. Hirschon, R. B. Wilson Jr., and R. M. Laine, *Appl. Catal.* (1987), 34, 311-316.
7. J. Shabtai, N. K. Nag, K. Balusami, B. Gajjar and F. E. Massoth, *Amer. Chem. Soc. Div. Pet. Prepr.*, 31 (1986) 231.
8. J. Shabtai, N. K. Nag and F. E. Massoth, *J. Catal.*, 104 (1987) 413.
9. T. G. Harvey and T. W. Matheson, *J. of Catal.*, 101, (1986) 253-261.
10. S.-M. Koo, M. L. Hoppe, and R. M. Laine, *Amer. Chem. Soc. Div. Pet. Prepr.* (1992), 37(1), 290-297.
11. I. Yermakov, *Catal. Rev.-Sci. Eng.*, (1976), 13, 77-120.

Table 1

TURNOVER FREQUENCIES FOR QUINOLINE FOR QUINOLINE HDN^a
USING PROMOTED CATALYSTS

| No. | Catalyst | TF ^b | | |
|-----|----------|-----------------|-----|-----|
| | | THQ | PCH | PB |
| 1 | CoMo | 54 | 8.9 | 0.5 |
| 2 | RuCoMo | 141 | 27 | 8.0 |
| 3 | NiMo | 86 | 15 | 1.7 |
| 4 | RuNiMo | 128 | 14 | 5.5 |

^aReaction of 10 mL of 0.197 M quinoline in n-hexadecane and 0.100 g of sulfided catalyst at 350°C and 500 psi H₂.

^bTF = moles reactant or product/mol Metal/h.

Table 2

SELECTIVITY AT 5 mol % CONVERSION^a

| No. | Catalyst | % PCH | % PB | % PCHE | PCH/PB |
|-----|----------|-------|------|--------|--------|
| 1 | CoMo | 82.2 | 4.6 | 13.2 | 17.8 |
| 2 | RuCoMo | 76.6 | 23.4 | 0 | 3.3 |
| 3 | NiMo | 73.3 | 14.9 | 11.8 | 4.9 |
| 4 | RuNiMo | 71.5 | 27.5 | 1.0 | 2.6 |

^aReaction of 10 mL of 0.197 M quinoline in n-hexadecane and 0.100 g of sulfided catalyst at 350°C and 500 psi H₂.

Table 3
EFFECT OF METHOD OF PREPARATION OF RuMo CATALYST
FOR QUINOLINE HDN^a

| No. | Method | TF ^b | | |
|-----|---|-----------------|-----|-----|
| | | THQ | PCH | PB |
| 1 | Ru/O ₂ /H ₂ S ^c | 50 | 0.3 | 0.1 |
| 2 | O ₂ /Ru/H ₂ S ^d | 67 | 14 | 2.3 |
| 3 | O ₂ /H ₂ S/Ru/H ₂ S ^e | 180 | 48 | 11 |

^aReaction of 10 mL of 0.197 M quinoline in n-hexadecane and 0.100 g of sulfided catalyst at 350°C and 500 psi H₂.

^bTF = moles reactant or product/mol Metal/h.

^cRu added to calcined Mo, calcining Ru, and then sulfiding.

^dRu added to calcined Mo, and then sulfiding.

^eRu added to sulfided Mo, and sulfided again.

Table 4
SELECTIVITY AT 5 mol % CONVERSION^a

| No. | Method | % PCH | % PB | % PCHE | PCH/PB |
|-----|---|-------|------|--------|--------|
| 1 | Ru/O ₂ /H ₂ S ^b | 63 | 21 | 16 | 3.0 |
| 2 | O ₂ /Ru/H ₂ S ^c | 80 | 14 | 6 | 5.7 |
| 3 | O ₂ /H ₂ S/Ru/H ₂ S ^d | 75 | 21 | 4 | 3.6 |

^aReaction of 10 mL of 0.197 M quinoline in n-hexadecane and 0.100 g of sulfided catalyst at 350 C and 500 psi H₂.

^bRu added to calcined Mo, calcining Ru, and then sulfiding.

^cRu added to calcined Mo, and then sulfiding.

^dRu added to sulfided Mo, and sulfided again.

Table 5
EFFECT OF CATALYST ON HYDROTREATMENT OF COAL TARs

| Run No. | Catalyst Type | HDN | | | Hydrogenation | | | Selectivity Kn/ Δ H/C |
|---------|---------------------|---------------------|----------------------|-----------------|---------------------|------------------|---------------------------|---------------------------------|
| | | N(wt%) ^a | DNR (%) ^b | Kn ^c | C(wt%) ^a | H/C ^d | Δ H/C ^e | |
| 1A | NiMo | 0.43 | 57.8 | 0.43 | 91.37 | 1.00 | 0.31 | 1.39 |
| 1B | RuNiMo | 0.33 | 67.6 | 0.55 | 90.62 | 1.07 | 0.38 | 1.45 |
| 2A | CoMo | 0.38 | 62.7 | 0.47 | 91.24 | 1.06 | 0.37 | 1.27 |
| 2B | RuCoMo | 0.42 | 58.8 | 0.44 | 91.16 | 1.06 | 0.37 | 1.19 |
| 3A | RuMo-3 ^f | 0.40 | 60.8 | 0.46 | 90.61 | 1.08 | 0.39 | 1.17 |
| 3B | RuMo-1 ^g | 0.54 | 47.1 | 0.32 | 91.82 | 0.93 | 0.24 | 1.33 |

^aWt % in product.

^bDegree of nitrogen removal.

^cRate of nitrogen removal hr⁻¹.

^dMole ratio.

^eH/C(product)-H/C(feed).

^fMo(sulfided) + Ru.

^gMo + Ru, then sulfided.